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Structural Ordering and its Correlation to the Optoelectronic Properties of a-Si:H Films

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ABSTRACT

Magnetic susceptibility (χ) was suggested theoretically to be sensitive to the overall structural order of a-Si:H. χ is measured precisely for various a-Si:H thin films using a new technique. The measured χ is shown to be sensitive to variations of the structural order and correlates well with the optoelectronic properties as well as the reversible conductivity changes, the SWE. Measurements of χ, H microstructure, and light-induced photoconductivity degradation on the same piece of thin film reveal clearly that the overall structural order plays an important role in the electronic properties including metastability of a-Si:H.

I. Introduction

The light induced defect creation was found to be smaller in a-Si:H films prepared by hot-wire chemical vapor deposition (HW-CVD) and by plasma-enhanced chemical vapor deposition (PE-CVD) under hydrogen dilution condition [1,2]. It was suggested that it is due to an improvement of the structural order[1-4]. This implies that the overall structure order of the film can be controlled and it has a direct impact to the metastability. Whereas, the electronic properties and its stability depends not only on deposition conditions but also sample thickness and substrate etc. The small difference of structural order among those device-quality films can hardly be detected by XRD and Raman spectroscopy [3,5]. Thus, more sensitive measures of overall structural order, especially those that could correlate with the SWE of a-Si:H, are highly desirable.

Previous studies have shown that the magnetic susceptibility χ is about a factor of 4.5 larger in a-Si than that in c-Si [6] due to structural deviations such as bond-angle and bond-length disorder[7]. In this work, we study χ in a series of HW a-Si:H films by using a new technique of NMR[8]. The goal is to detect possible differences in χ between device-quality a-Si:H films which exhibit different levels of metastability. Conventional techniques for measuring χ such as SQUID magnetometer, find some difficulties because of the small amount of sample (0.5 mg) and the irreproducibility of the background signal intensity after sample changes. In this work, the ^{1}H resonance frequencies are measured for sample orientations with the film surface both perpendicular and parallel to the external magnetic field. The change of the resonance frequency with such change of sample orientation gives a direct measure of χ.[8]. Theoretically, the structural order is measured by the contribution to the susceptibility per Si-Si bond [7]. Because of the possible existence of nanovoids, molar susceptibility, $\chi_{mol}=m\chi/4\pi\rho$ is a more appropriate measure of the local structural order, where ρ=2.300 g/cm^3 is the film's mass density and m =28 g/mol, is the silicon's molar mass.

II. Experimental and Results

1-μm thick a-Si:H films were deposited on 1.5x1.5 cm^2, 0.042 cm-thick quartz substrates by HWCVD with pure silane. A μc-Si sample #8 was prepared with H dilution. A single piece of sample is placed in a flattened NMR coil. The coil could be oriented so that the sample would be at any desired angle with respect to the external magnetic field. The NMR spectra were obtained in a field of 4.7 Tesla at room temperature. Since the films studied have low H contents, the home-made ^{1}H-NMR probe was specially designed to have very little or no ^{1}H background signal.

Table I
Sample preparation parameters and the measured χ_{mol}

Sample ID	T_S (^{o}C)	T_{fil} (^{o}C)	Growth Rate (Å/s)	C_H (at.%)	χ_{mol} (10^{-6}cm^3/mol)
1	280	1500	7.5	4.5	-13.27±0.49
2	310	1500	7.7	4.1	-13.76±0.59
3	340	1500	7.7	3.3	-13.72±0.64
4	360	1500	6.9	3.6	-12.72±0.48
5	380	1500	8.2	2.4	-13.92±0.54
6	380	1500	5.4	4.4	-11.62±0.56
7	380	1800	8.4	4.0	-13.73±0.53
8	220	1800	6.4	6.3	-6±0.8

The H microstructure were characterized by the NMR spectra which consist of a broad Gaussian line with a full width at half height (FWHH) of about 40 kHz (200 ppm) and a narrow Lorentzian line of about 3 kHz (15 ppm), due to clustered and isolated monohydrides (Si-H), respectively. The measured values of the molar susceptibility are listed in Table I. T_s and T_{fil} are the substrate and filament temperatures. χ_{mol} is in the cgs unit cm^3/mol. A μc-Si:H film yields a much smaller average χ_{mol}; here, the value of χ_{mol} implies a ~70% volume fraction of crystallites, which is consistent with the growth conditions.

Figure 1 shows the measured χ_{mol} vs. the growth rate for the films listed in Table I. The largest variation in χ_{mol}

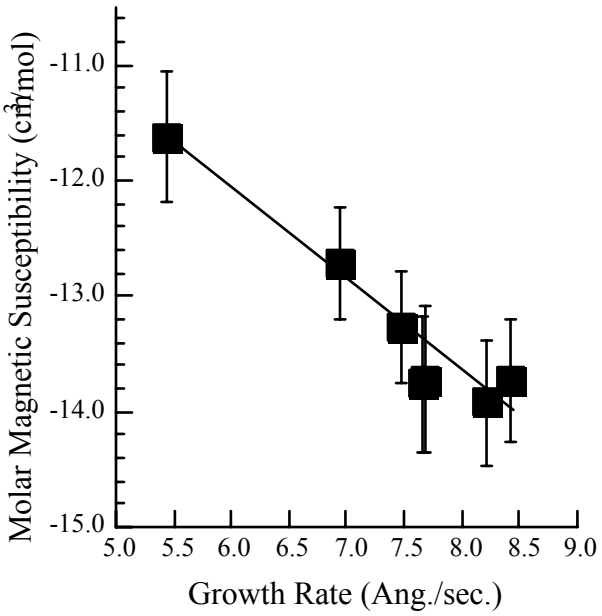

Figure 1
Measured χ_{mol} versus the growth rate for all the a-Si:H films listed in Table I.

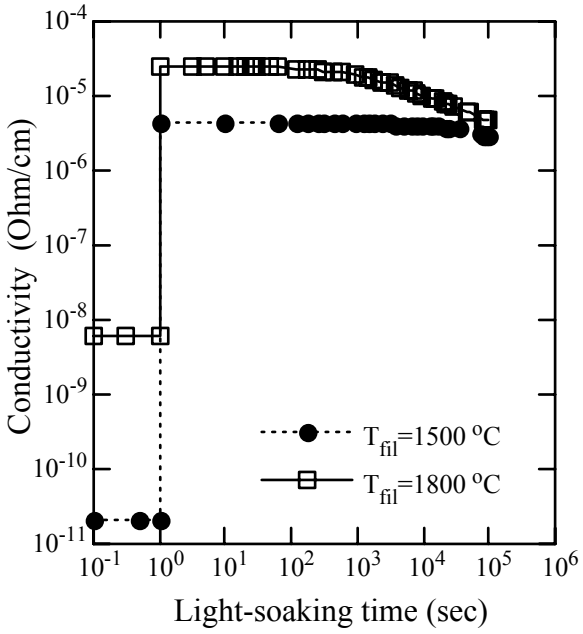

Figure 2
Dependence of the photoconductivity on light-soaking time for samples #6 and #7.

is about 17%. The data implies that in this growth parameter regime, a lower growth rate leads to a more ordered amorphous Si network. No such correlation is found between χ_{mol} and T_s or H content in this range of T_S (280 -380 ^{O}C). Fig. 2 shows the dependence of the phto-conductivity on light-soaking time, under 150 mW/cm^2 white light, in vacuum at 310 K, for films #6 and #7. For sample 6, which has the lowest χ_{mol}, photoconductivity decreases by only a factor of 1.5 at saturation of 28 hr. Sample 7, which has a χ about 15% larger than that of sample 6, is significantly less stable; its photo-conductivity decreases by a factor of 5.3 after the same illumination. The initial photo-sensitivity of sample 6 is 2.1x10^5 which is fifty times larger than that of sample 7.

III. Summary

The NMR method provides a unique tool for precise measurement of magnetic susceptibility χ in thin films. Measurements of χ, hydrogen microstructure, and photodegradation carried out on the same piece of sample suggest that the overall structural order plays an important role in both the initial photosensitivity and in the metastability of a-Si:H. The observation that growth rate correlates with the overall structural order in a-Si:H is not surprising, since it is well known that lower growth rates generally lead to lower defect densities in such films[9]. This unique tool allows for the unambiguous identification of the importance of the overall structural order on the metastability of a-Si:H in thin-film device structures.

Acknowledgments

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